

METAL SEMICONDUCTOR BARRIER  
HEIGHT STUDIES ON ZnSe

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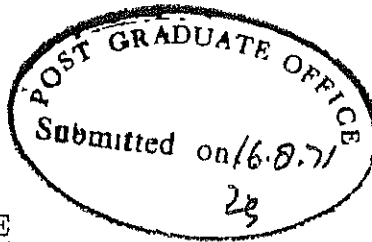
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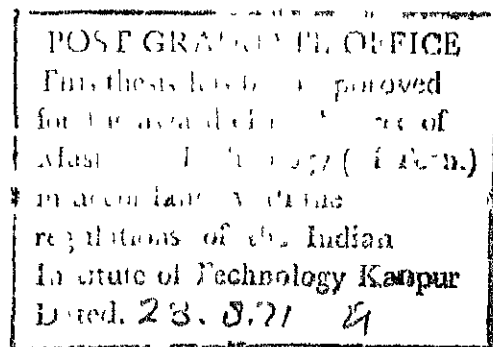
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CERTIFICATE

This is to certify that this work on "Metal Semiconductor Barrier Height Studies on ZnSe" has been carried out under my supervision and it has not been submitted elsewhere for a degree.

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## ABSTRACT

Barrier height measurements were performed on ZnSe, using high purity metals. C-V measurements were used for finding barrier height of the barrier between the metal and the semiconductor. Barrier height was found to increase linearly with the electronegativity of the metal. Value of 'n' equal to  $1.1 \pm 0.02$  was found for the forward characteristic of the diodes. The reverse characteristics could be explained in terms of image force lowering of barrier height.

Ohmic contacts to ZnSe crystals have been made using In or 25% In-Ga. Using 25% In-Ga alloy, a resistance of 5 ohm was obtained between two metal dots alloyed to ZnSe of 0.25 oh m. cm. resistivity.

# CHAPTER 1

## INTRODUCTION

Considerable interest has recently been shown in metal-semiconductor junction, prompted by new device applications such as metal base transistors, nuclear particle detectors, varactor diodes, etc. Also, in many semiconductor devices, surfaces control the performance and stability of the device, and metal-semiconductor contact has been found to be a useful tool in the study of surface properties. It gives us the understanding about the band and defect structure near and at semiconductor surfaces, and the transport of charge carriers across interfaces of solids.

A wealth of literature is available on metal-semiconductor system using group IV and III-V compound semiconductors, while little attention has been devoted to II-VI compounds. One of the major issues, at present, is the extent to which the height of the Schottky barrier,  $\phi_B$ , depends on the workfunction of the metal (see Figure 1),

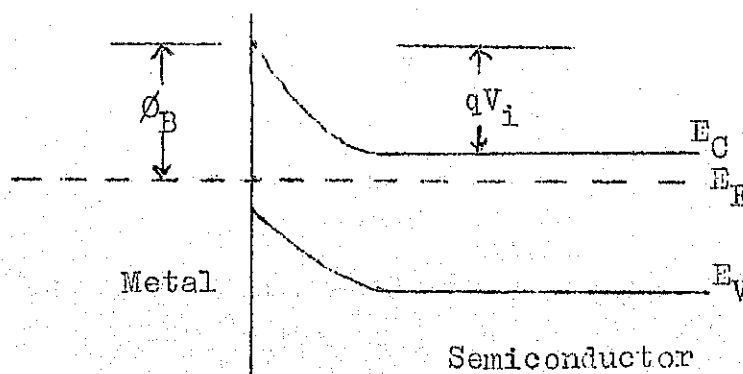


Figure 1.1: Band diagram of metal-semiconductor contact showing definition of  $\phi_B$  and  $V_i$ .

According to the simple theory<sup>1</sup>, the barrier height is given by the relationship

$$\phi_B = \phi_M - X_S \quad (1)$$

where  $\phi_M$  is the workfunction of the metal and  $X_S$  is the electron affinity of the semiconductor. However, in 1947, as a result of early measurements which showed  $\phi_B$  to be largely independent of  $\phi_M$ , Bardeen<sup>2</sup> proposed an extension of the theory by taking surface states into account. According to Bardeen's theory,  $\phi_B$  should be almost independent of  $\phi_M$  if the density of surface states is very high.

Si and GaAs were found to follow the Bardeen model. Later, results by Spitzer and Mead<sup>3</sup> and Goodman<sup>4</sup> showed that CdS gave results in agreement with Eq.(1). Mead and Spitzer presented results for a large number of additional systems. They found that Column IV and III-V semiconductors followed the Bardeen model, with pinning of the Fermi level at 1/3 the gap energy above the valence band edge. Of the two II-VI compounds reported, CdS obeyed Eq.(1), while CdTe showed pinning of the Fermi level slightly above the middle of the gap.

Quite recently, Mead<sup>5</sup> has reviewed an extensive data and concluded that semiconductors can be broadly classified into two categories, those in which surface



states play an important role and those where surface states play a negligible role. According to him, ionically bonded materials would have few localized states in the forbidden gap, and hence follow Eq.(1), while covalently bonded crystals would have a high density of states in the gap and consequently would exhibit pinning of the Fermi level.

Aven and Mead<sup>6</sup> found that metal contacts to ZnS behaved according to Eq.(1), but replaced  $\phi_M$  by the electronegativity of the metal,  $X_M$ . Further results on ZnO and ZnSe, reported by Mead<sup>7</sup>, again showed  $\phi_B$  proportional to  $X_M$ , although only three points were given for ZnSe. More recently, Swank et.al.<sup>8</sup> have also found barrier height on ZnSe proportional to the electronegativity of the metal, with exception of highly reactive metals such as Mg, Ca, and Ba.

Swank<sup>9</sup> measured the electron affinities of many II-VI semiconductors photoelectrically, and found agreement with Eq.(1) for a few barrier height measurements. This paper also reported band bending at the clean surface, indicating pinning of the Fermi level by surface states near the band edges. It was suggested perhaps in the II-VI compounds, the surface states form two bands near the band edges with a gap in between. Such a model had been suggested on other

grounds by Levine and Mark<sup>10</sup>. If a similar distribution is present in the metal semiconductor system, one might expect  $\phi_B$  to obey Eq.(1). over a certain range of  $\phi_M$ , but be pinned by interface states when the Fermi level entered the region occupied by them.

Since ZnSe has a wide band gap, and also a large band bending at the free surface, one might expect to see such effects in this material. It was the objective of the present work to test the validity of this concept.

Another purpose of the present research work was to provide <sup>ohmic</sup> contacts to ZnSe. It has been found difficult to make good ohmic contacts to this material because of the following reasons:

(a) requirement of a low temperature fabrication method as at temperatures above 400°C Zn outdiffusion from the surface leaves an insulating layer on the surface.

(b) difficulty in finding suitable metals which provide good wetting of the semiconductor surface at temperatures below 400°C.

## CHAPTER 2

### IMPORTANT PROPERTIES OF ZnSe

The interest in ZnSe is of more recent origin and, consequently, the amount of work reported on this semiconducting compound is considerably less.

Zinc Selenide crystals with the Zinc blende arrangement grow from the vapor at 1120 - 1200°C; faulted or mixed crystals can be obtained at 1050 - 1080°C and they may be transformed to cubic by annealing at 900°C.<sup>11</sup> The Wurtzite modification has been prepared but there are conflicting values reported for the hexagonal cell constants. Korneeva<sup>12</sup> has been able to synthesize hexagonal ZnSe by decomposing ZnSe-N<sub>2</sub>H<sub>4</sub> at 400°C.

Zinc Selenide is a light, yellow semiconducting material, and it can be polished to a mirror like finish. It is usually found of n-type. Some of the properties of ZnSe are shown in Table 2.1.

#### Doping of ZnSe:

ZnSe may be doped n-type with Al, Ga or In to resistivities in the range of 0.02 to 1.0 ohm cm., with mobilities of 200-500 cm<sup>2</sup>/volt. sec., provided measures are taken to suppress Zn vacancies. Thin films of

Table 2.1  
Properties of ZnSe

Unless otherwise indicated, these properties represent data taken at 300°K			
Atomoc number of constituents	Zn Se	30 34	
Melting points of constituents at one atmospheric pressure	Zn Se	420°C 217°C	
Boiling points of constituents at one atmospheric pressure	Zn Se	908°C 685°C	
Dielectric constant		8.66 <sup>13</sup>	5.9 <sup>14</sup>
Energy gap		2.7 eV	
Temperature coefficient of energy gap <sup>15</sup>		-8x10 <sup>-4</sup> eV/°K	
Melting point		1520°C	
Maximum electron lattice mobility		530 cm <sup>2</sup> /V-sec.	
Refractive index <sup>14</sup>		2.43	
Lattice Constant <sup>16</sup>		Covalent 2.45°A	Ionic 2.55°A Expt. 2.46°A
Effective mass <sup>15</sup>	Electron Hole	0.17 m Kg. 0.6 m Kg.	m=9.1x10 <sup>-31</sup> Kg.
Effective density of states		1.75x10 <sup>18</sup> /c.c.	

supposedly 50 ohm-cm p-type ZnSe have been reported<sup>17</sup>, but in general p-type doping of ZnSe has not been achieved by workers with this material.

Diffusing n-type impurities into ZnSe usually promotes heavy self compensation by indiffusing Zn vacancies. The Zinc vacancy is a double acceptor capable of consuming the electrons of two donor atoms. The more donor atoms in the lattice, the more Zinc vacancies are formed. A dopant atom may pair up with a zinc vacancy to form a Zincvacancydopant complex, which is an acceptor. This complex in turn compensates any dopant atoms left. In many cases the self compensation is so great that the concentration of donor atoms may be  $10^{19} \text{ cm}^{-3}$  and the electron concentration will be only  $10^{17} \text{ cm}^{-3}$ . Zinc vacancy formation in ZnSe becomes more complete at higher temperatures and is a serious problem above 400°C.

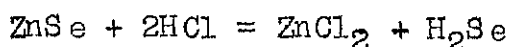
For doping, ZnSe is submerged in molten Zinc plus dopant for a time sufficient to achieve uniform doping. The Zinc suppresses any Zinc outdiffusion from ZnSe and helps provide Zinc diffusion into the crystal to eliminate Zn vacancies.

#### Surface film on ZnSe Surface:

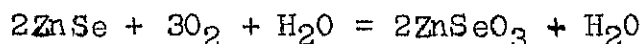
It has been reported by Yep et.al.<sup>18</sup> that every chemical treatment of ZnSe surface leaves a remanent

film on the surface. The thickness of this film is strongly dependent upon the type of surface treatment; etching in HCl was found to leave the thickest film. Etching in Br-Methanol reduces the film thickness on an unetched polished and solvent-clean surface, the film thickness is found to be somewhere from 20-50°A.

Concerning the composition of the insulating film no information is available in the literature. However, judging from the nature of the treatment given to obtain clean surface and to make alloyed contacts to ZnSe it appears that the film contains oxides of Zn and Se, probably along with Selenides of Zn<sup>30</sup>. When ZnSe is etched with HCl the following reaction takes place.

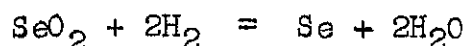


Both these compounds are soluble in methanol. Now during this etching process and probably also after etching, ZnO and SeO<sub>2</sub> are formed on the surface along with some ZnSeO<sub>3</sub>. According to Mellor<sup>19</sup>, oxygen reacts with ZnSe in the presence of moisture.

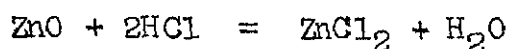


This compound which is probably formed at ZnSe surface is insoluble in water and alcohol. The surface of ZnSe therefore may contain ZnO, SeO<sub>2</sub> and ZnSeO<sub>3</sub>. Now during the alloying process when the sample is heated to about

200°C,  $\text{ZnSeO}_3$  first loses the absorbed water and then decomposes leaving  $\text{ZnO}$  as residue. When  $\text{SeO}_2$  is heated in hydrogen it is reduced to metallic Se.



$\text{ZnO}$  on the other hand is not reduced by hydrogen at least up to 400°C, so that passing of  $\text{H}_2$  does not remove  $\text{ZnO}$  film. However, nascent hydrogen, can react with  $\text{ZnO}$  and so the film can be removed. Now what happens when  $\text{HCl}$  flux is used? Dry  $\text{HCl}$  does not have any reaction with  $\text{ZnSe}$  but  $\text{ZnO}$  reacts with it at a temperature of



$\text{SeO}_2$  forms hydroxychlorides in dry  $\text{HCl}$ , i.e.,  $\text{SeO}_2 \cdot 2\text{HCl}$  and  $\text{SeO}_2 \cdot 4\text{HCl}$ . Both these compounds evaporate above 170°C with slight decomposition. If neither  $\text{H}_2$  nor  $\text{HCl}$  is used then these oxides cannot be removed except probably at very high temperatures.

Now coming to the etching with  $\text{H}_2\text{SO}_4 + \text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{ZnSe}$  is only slightly attacked by  $\text{H}_2\text{SO}_4$  but  $\text{K}_2\text{Cr}_2\text{O}_7$ , probably reacts with Se atoms to give  $\text{SeO}$  which is very soluble in  $\text{H}_2\text{SO}_4$ .  $\text{K}_2\text{Cr}_2\text{O}_7$  reacts with  $\text{ZnO}$  to produce  $\text{ZnCrO}_4$ . This compound is bright yellow and is soluble in acids. Other impurities left on the surface probably Se (which is recognized by its orange red color) and sulphates of Zn are dissolved in  $\text{KCN}$ . Selenium forms

KSeCN and Zn also forms complex cynides with KCN. These complex cynides are removed by hot water.

The idea of  $\text{NH}_4\text{Cl}$  used as a flux also support the view that ZnO is one of the important constituents of the surface film. ZnO dissolves readily in  $\text{NH}_4\text{Cl}$  solution.



### CHAPTER 3

#### OHMIC CONTACTS TO ZINC SELENIDE

It is necessary to make electrical contact to semiconductor crystals by means of metallic conductors in order to carry out electrical measurements or to fabricate useful semiconductor devices.

Phenomenologically, an ohmic contact is defined by the fact that it obeys ohm's law, thus fulfilling the following two requirements: (a) the threshold voltage for zero current is negligible with respect to the applied voltage (b) the proportionality factor between voltage and current (i.e., the conductivity) does not vary measurably with voltage. (a) and (b) must be valid within a certain not too small voltage range, say from about 1 mV to several volts.

Another way to describe an ohmic contact to a semiconductor is in terms of its particular application. The contact should not add a significant parasitic impedance to the structure on which it is used, and it should not alter the equilibrium carrier densities within the semiconductor sufficiently to change the device characteristics. Moreover, it should allow the current carriers to pass across the transition region without

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introducing any modification into them i.e. it should not inject carriers into the device or hinder the motion of carriers at the transition region; furthermore, the resistance and the properties of the contact should not change with ambient and should also be stable at different temperatures. Contact should also be mechanically strong to support the device. It should be as noise free as possible.

Although the problem of making ohmic contact has been solved empirically in most cases of technologically important semiconductors, some of the general requirements for obtaining ohmic contacts are following:

(i) the desirability of a low potential barrier which in the ideal case should be zero,

(ii) the need to avoid high resistivity intervening compounds between the metal and the semiconductor,

(iii) the advisability of a heavily doped layer under the semiconductor.

#### Models Used to Explain Ohmic Contact:

Neglecting space charge effects in the bulk of semiconductor, (an ideal ohmic contact will be present) if the voltage drop at the electrodes, which is required to supply a number of mobile charge carriers to the semiconductor sufficient to maintain the carrier

*1. ideal?*

concentration essentially constant, is small compared with the total voltage drop across the semiconductor.

This may be the case if the workfunction of the metal is equal to or smaller than the workfunction of the semiconductor i.e.  $\phi_M \leq \phi_S$  as shown in Figure 3.1, in case the semiconductor is of n-type. If the semiconductor is of p-type, the workfunction of the metal should be equal to or larger than the workfunction of the semiconductor i.e.  $\phi_M \geq \phi_S$  as shown in Figure 3.2. This Model is sufficient for explaining ohmic contacts, if metal and semiconductor are in intimate contact. However, it cannot explain ohmic contacts made on semiconductor surfaces which have been previously damaged by lapping or ion bombardment. In this case, any metal irrespective of its work function is found to make an ohmic contact. Figure 3.3 shows the energy diagram of such a contact. Ohmic nature of this contact can be explained if we take the analogy of a p-n junction having a transition region where the lifetime of current carriers is so short that thermodynamic equilibrium can be maintained throughout the transition region thickness. Such a p-n junction has no barrier and its transition region becomes merely a region of high resistivity without any rectifying properties.

Workfunction criterion of explaining ohmic contact is also meaningless in case of contact metals which, when

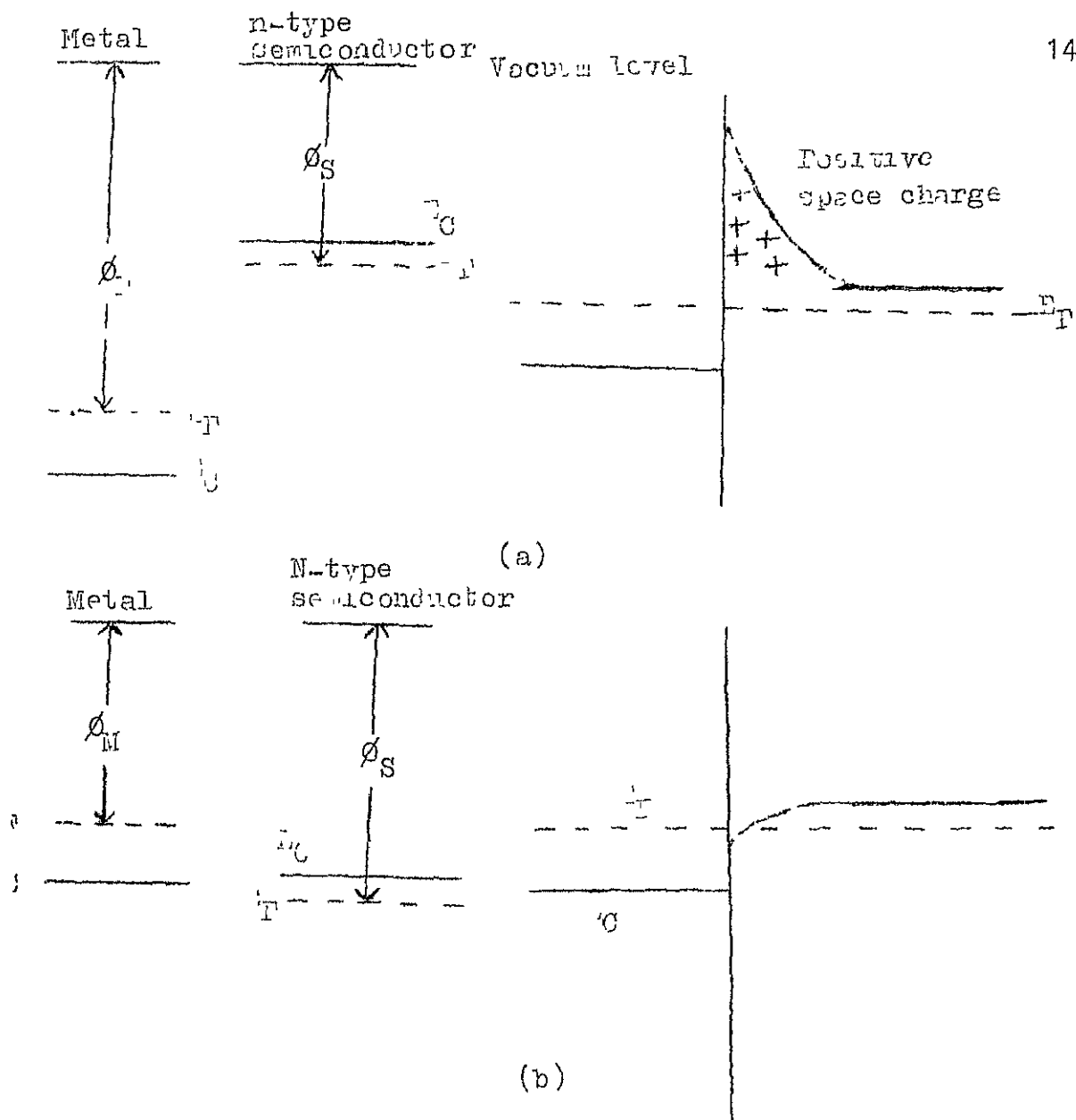
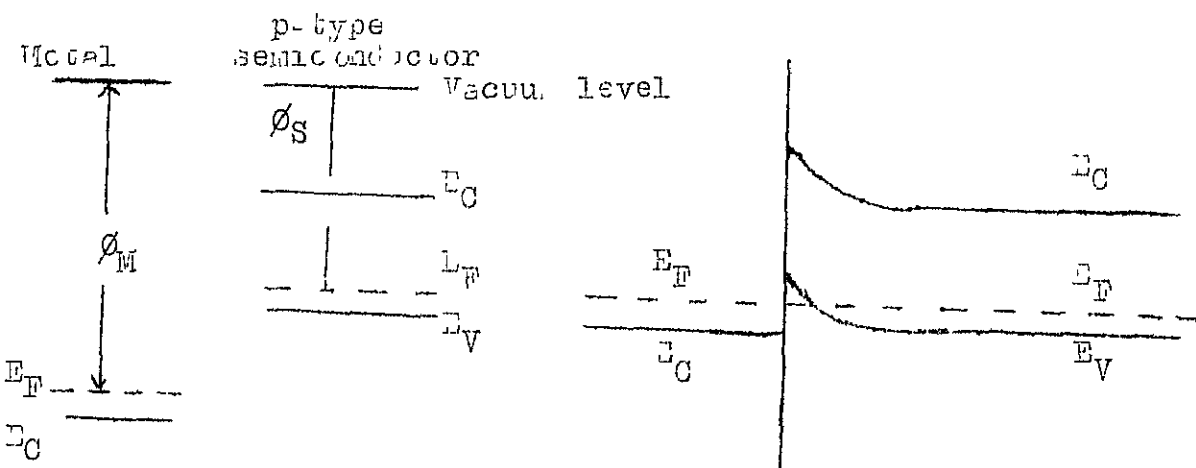


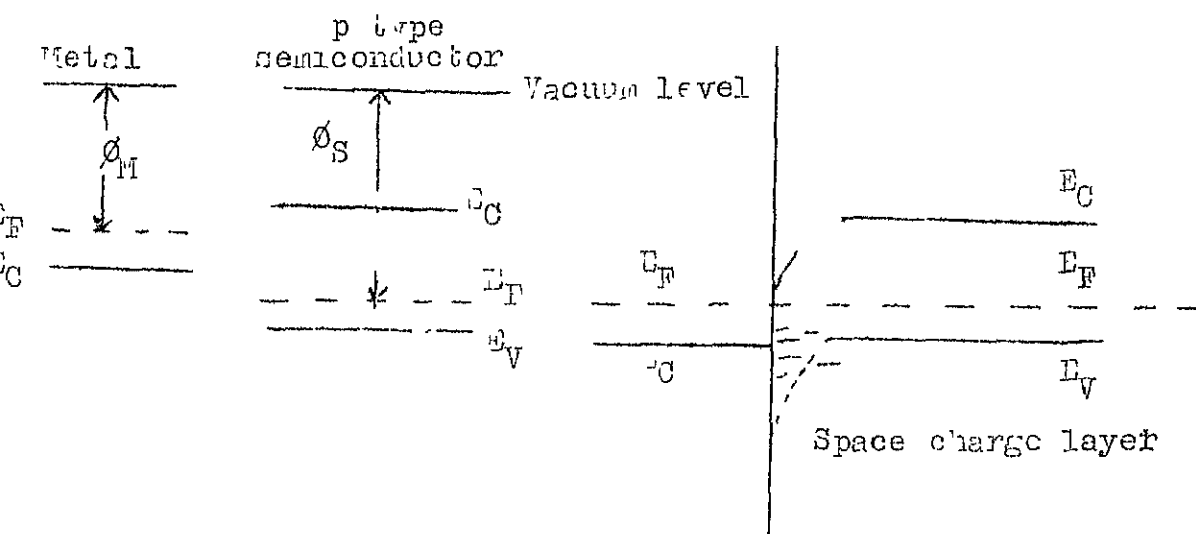
Figure 3.1: Metal and n type semiconductor contacts

(a)  $\phi_M > \phi_S$  , Rectifying contact

(b)  $\phi_M < \phi_S$  , ohmic contact.



(a)



(b)

Figure 3.2: Metal and p type semiconductor contacts.

(a)  $\phi_M > \phi_S$ , ohmic contact

(b)  $\phi_M < \phi_S$ , rectifying contact.

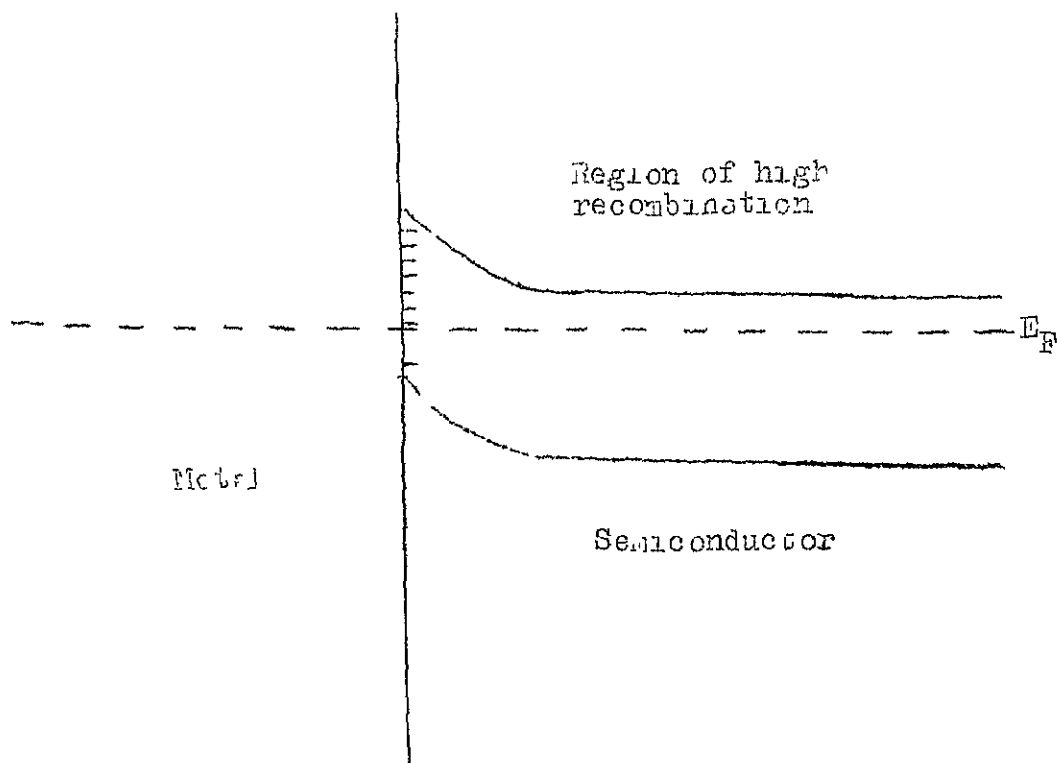


Figure 3.3: Contact between a metal and a damaged semiconducting surface.

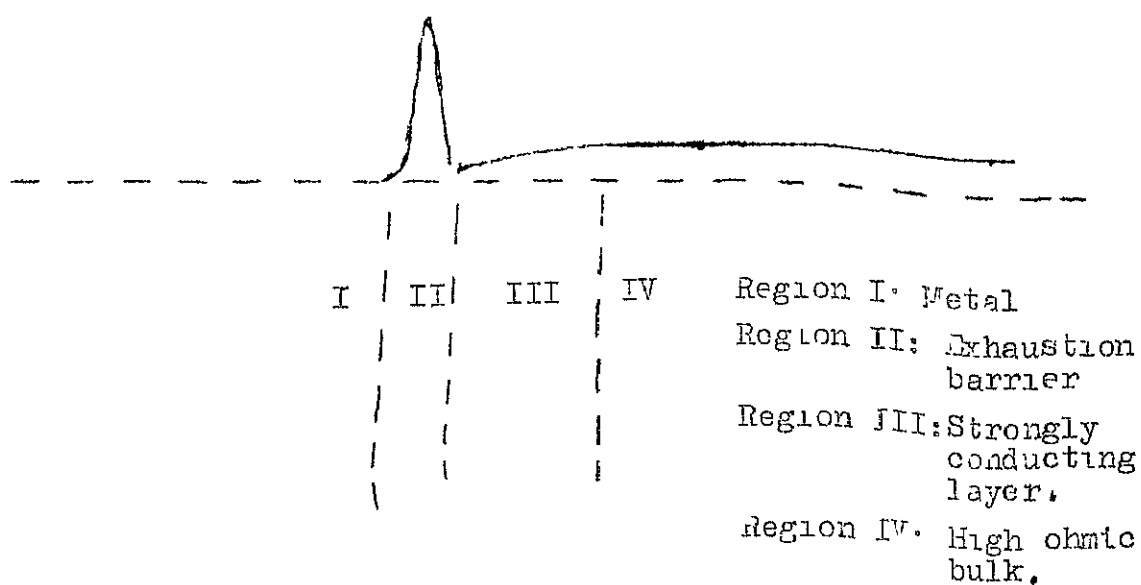


Figure 3.4: Ohmic contact between a highly resistive n type semiconductor and a metal having a work function larger than that of semiconductor.

Although both these conditions are favourable for making ohmic contacts, it is found in practice that the alloyed In contacts are not very satisfactory<sup>23</sup>. It is probably due to the presence of a thin insulating layer on the surface of ZnSe. This layer is probably unaffected by heat treatment upto 300°C. As the temperature exceeds 400°C the outdiffusion of Zn atoms becomes very rapid<sup>24</sup> and the Zn vacancies compensate any donor atoms that come from In metal. Thus heavy doping of the ZnSe surface becomes impossible. In order to avoid this difficulty use has been made of fluxes that clean the surface and provide better wetting of the ZnSe by In. Though most of the alloying work has been done in a H<sub>2</sub> atmosphere the wetting has not been good at temperatures below 400°C. Use of solid fluxing such as NH<sub>4</sub>Cl<sup>23</sup> and InCl<sub>3</sub>-NH<sub>4</sub>Cl<sup>22</sup> has been found to improve the wetting considerably but still the contact quality was found to be poor. Use of 1-2% of high purity HCl gas in an Ar -15% H<sub>2</sub> atmosphere has been found to give reasonably good contacts as judged by their current voltage characteristics but further tests revealed that the contacts themselves possessed considerable resistance<sup>24</sup>. According to Feucht and Milnes<sup>24</sup>, HCl is supposed to clean the In dots and promote better wetting of the ZnSe. Ludwig<sup>23,25</sup> has reported that a thin layer of chemically deposited Ni on ZnSe surface etched in hot NaOH solution provides very good wetting of ZnSe by In at 300°C and the contacts obtained in this way were superior to those obtained otherwise.



Culow et.al.<sup>26</sup> have reported a method of making

In contacts where nascent hydrogen was used to clean the ZnSe surface. They placed a minute In cylinder on ZnSe — about 3 m.m. below a tungsten filament. The filament was heated to about 2000°C for a few seconds in a hydrogen atmosphere when the cylinder melted and alloyed to the surface making ohmic contacts. They believed that the heater created nascent hydrogen which cleaned the ZnSe surface and allowed the In to wet it.

Ludwig and Aren<sup>23</sup> used Al as a dopant to produce a low resistivity skin on the ZnSe surface. In their experiment, ZnSe wafers were heated by putting them in contact with molten Zn and 1% Al at 850°C for seven hours, but the contacts obtained on these samples were much inferior to those obtained by Ni plating. They attributed this inferior nature of the contacts to the formation of an insulating layer, the mechanism of which has not been properly understood.

#### Experimental:

In literature, we find that In has been mostly used to make ohmic contacts to ZnSe. All other metals have not been found useful for some or other reasons. For example, Al is eliminated because its melting temperature is 660°C which is much higher than 400°C.

The contact technology used in the present work involves alloying In or InGa at temperatures between 250°C and 400°C in an ambient of nitrogen.

An alloy stage was fabricated for making alloy contacts of In or In-Ga. A graphite strip was mounted on two electrodes, fixed on stainless steel base, through Teflon insulating bushes. The graphite strip was covered with a glass lid, and thus it was sealed from ambient with the help of this lid using a O-ring. An alumel-cromel thermocouple was inserted from bottom of the base plate and connected with graphite strip for measuring temperature of the graphite strip. Two holes were made in the base plate for taking in and taking out the inert gas. Non-corrodable tubing was used to transport the inert gas.

Before alloying ZnSe and the contact metal must be carefully cleaned. ZnSe chips are lapped with 15  $\mu$ , 5  $\mu$ , and 1  $\mu$  Alumina power in succession. These chips are then solvent cleaned, given a light etch in 1/2% bromine methanol, and stored in methanol until use.

For making ohmic contact, the etched sample was given a dip in dilute NaOH, before use. This helps in cleaning the surface of ZnSe and improve wetting. The sample is then placed on the Graphite strip and In or In-Ga dots placed on it. The glass lid is carefully

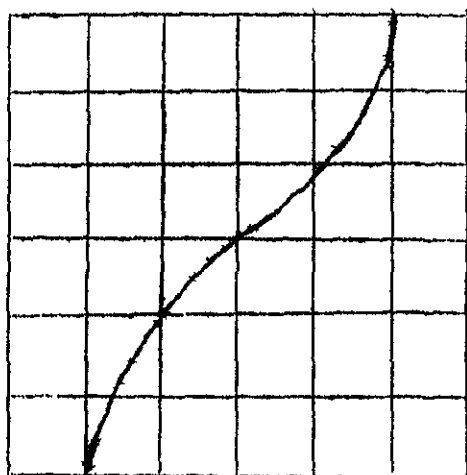
placed over the strip and sealed down. The volume under the lid is then purged by pouring nitrogen. After nitrogen brings out all the air present inside the lid, the strip temperature is raised very slowly to the alloy temperature. The system is held at the alloying temperature for about 15 to 30 seconds and then allowed to cool slowly.  $N_2$  is shut off.

It is important to raise and lower the temperature slowly. If this is not done, the In spheres roll around on the sample probably from thermal and mechanical agitation. When this occurs, contacts are found to be poor.

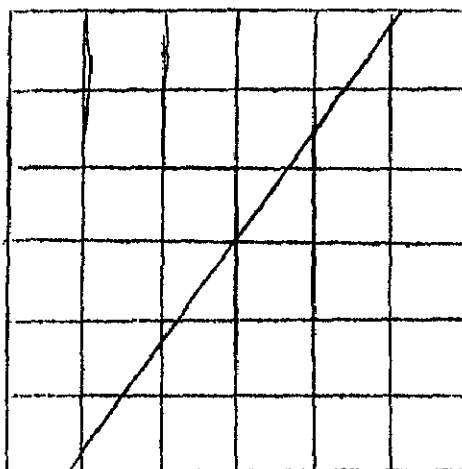
In spheres (20 mil dia) were thus alloyed with ZnSe chips, having different lapping finish. It was found that wetting of the sample was poor in all the cases, but it seemed to improve by fine lapping.

Next, some work on evaporated contacts was done. In was evaporated on ZnSe from Mo boat. After evaporation, the sample was put in the alloy stage and In was alloyed to ZnSe. Poor quality nonlinear contacts were observed.

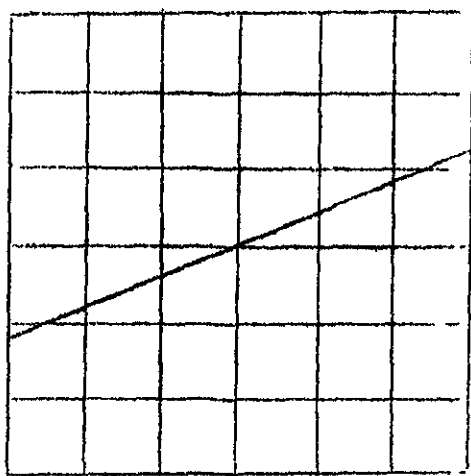
To improve wetting of ZnSe surface, the use of  $NH_4Cl$  powder was brought in. In dots were used surrounded by  $NH_4Cl$  powder. One difficulty was found that  $NH_4Cl$  powder and In dots slipped from the ZnSe sample due to thermal agitation, though all care was taken to increase the



(a)



(b)



(c)

Figure 3.5: I-V Characteristics of In contacts on ZnSe at 300°K.

- (a) 0.01 mA/cm Vert., 0.5 V/cm Hor., Alloyed at 350°C.
- (b) 1 mA/cm Vert., 0.05 V/cm Hor., Alloyed at 300°C using  $\text{NH}_4\text{Cl}$  flux layer.
- (c) 0.05 mA/cm Vert., 10 V/cm Hor., Alloyed at 300°C, In evaporated from inverted boat.

temperature slowly. To avoid this, ZnSe samples were dipped into saturated  $\text{NH}_4\text{Cl}$  solution made in distilled water. A layer of  $\text{NH}_4\text{Cl}$  sticks to the sample when it is brought out from the solution. In dots could be very well fixed into this layer of  $\text{NH}_4\text{Cl}$ . Wetting of In dots was found to be much better. A resistance of 35 ohms (as shown from the V.I. plot on curve tracer) was found between two 'In' dots.

At this point, we can compare this result into other results obtained by Teucht and Milnes<sup>24</sup>.

(300°K) ohm cm.	R(300°K) ohms
0.25	35
0.75 <sup>-</sup>	25
4.00 <sup>-</sup>	75

- Work of Teucht and Milnes.

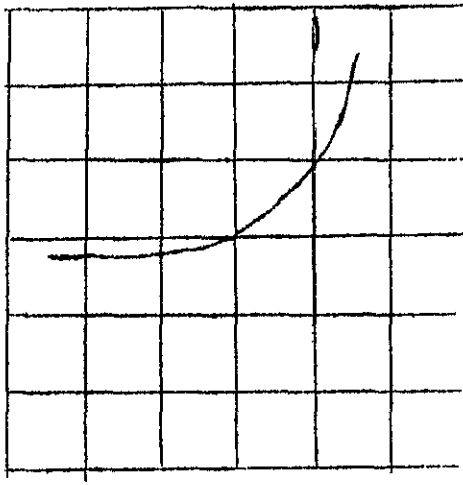
It is sure that good wetting is a function of the cleaning of the ZnSe surface. It was thought that some way should be evolved so that ZnSe is not exposed to atmosphere after cleaning.

For this, following experiment was conducted. The sample with  $\text{NH}_4\text{Cl}$  layer on it was placed on a Mo strip inside the vacuum chamber. Before this, the

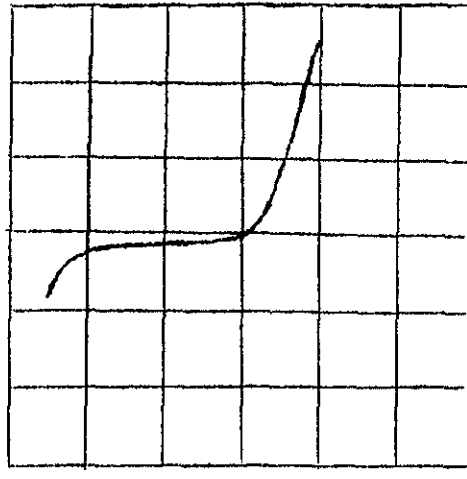
vacuum chamber was flushed with nitrogen. An inverted boat was put above the ZnSe sample; the inverted boat contained In. A shutter was placed between the ZnSe sample and the inverted boat. ZnSe sample was heated so that  $\text{NH}_4\text{Cl}$  evaporates leaving a clean surface underneath. The temperature of the sample was held at  $300^\circ\text{C}$ . At this time, the shutter was removed to let the In vapours strike the sample. The sample was cooled down and taken out of the vacuum chamber. Selective etching of In was done to get four contact areas of In Znse sample. The experiment was not a success, and the contact resistance between two contacts was very high; though linear.

Work with In-Ga alloy was started at this stage. Ga was sure to give good wetting on ZnSe surface. 25% In-Ga eutectic was used which is liquid at room temperature; it was prepared by mixing 25% of In and 75% of Ga by weight. By putting these two metals in boiling water, they mix readily. This alloy can be etched in HF diluted with HCl. Small dots of this liquid alloy can be very easily made and presented for a few hours in a cold place.

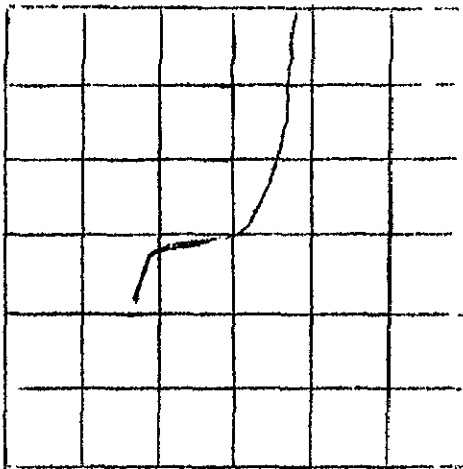
Alloy contacts on ZnSe were fabricated using 25% In-Ga at temperatures between  $250^\circ\text{C}$  and  $400^\circ\text{C}$ . Contacts were found to be nonlinear when alloyed at



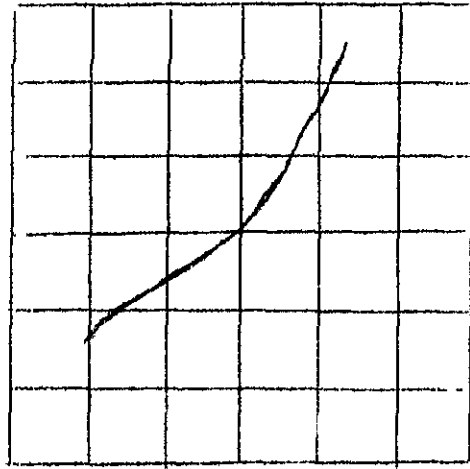
(a)



(b)



(c)



(d)

Figure 3.6: I-V characteristics of In-Ga contacts on ZnSe at 300°K.

(a) 0.1 mA/cm. Vert., 2 V/cm. Hor., Alloyed at 250°C for 1/2 minute.

(b) 0.1 mA/cm Vert., 2 V/cm. Hor., Alloyed at 250°C for 1 minute.

(c) 0.1 mA/cm., Vert., 2 V/cm. Hor. Alloyed at 250°C for 1 1/2 minutes.

(d) 0.1 mA/cm. Vert., 1 V/cm. Hor., Alloyed at 250°C for 2 minutes.

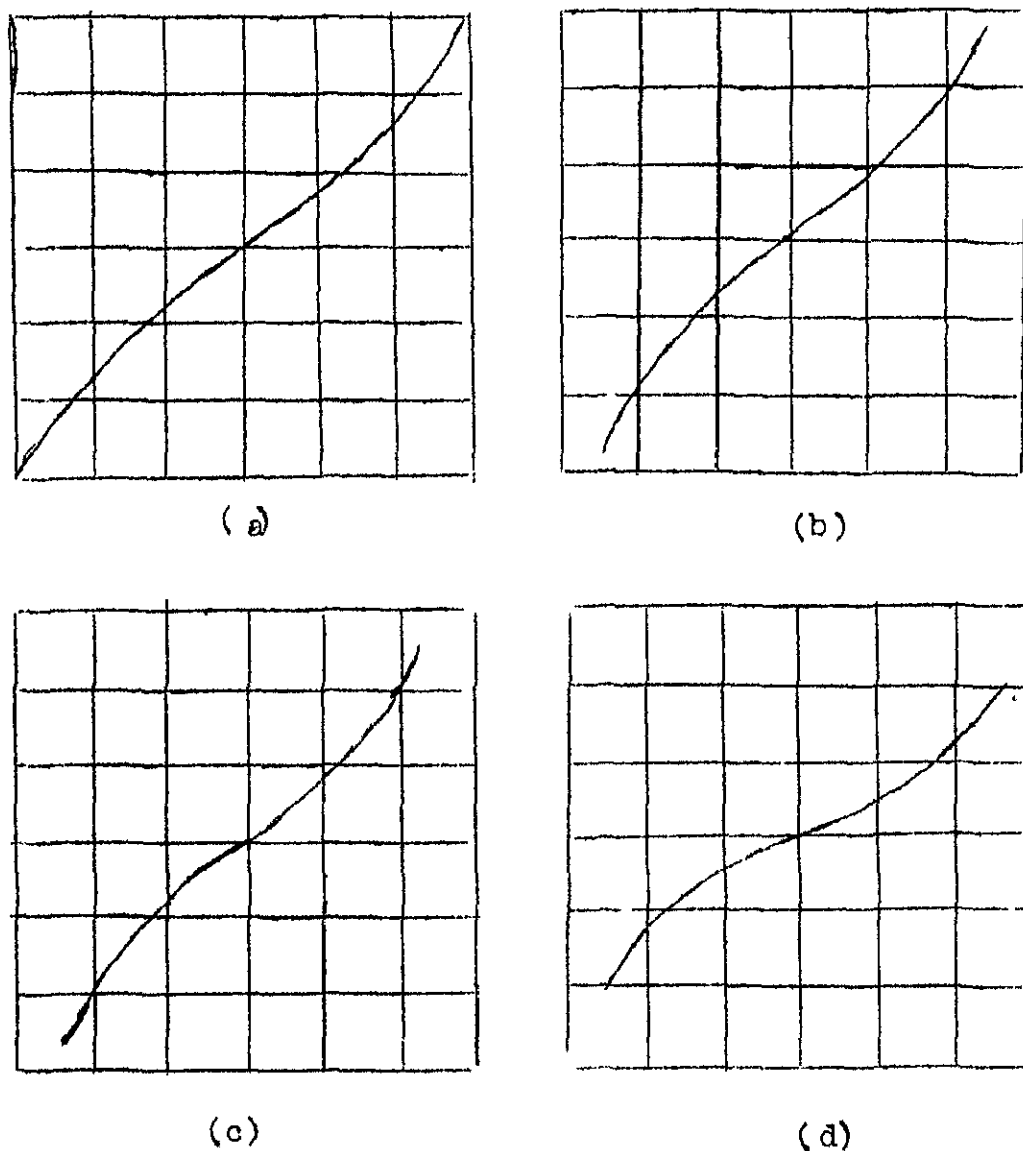
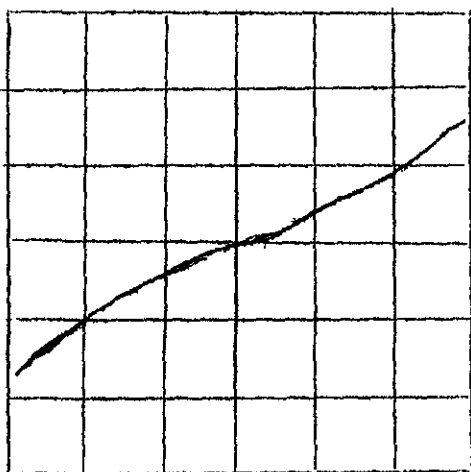


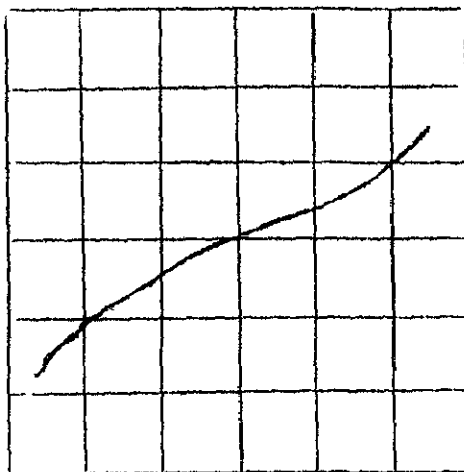
Figure 3.7 I-V Characteristics of In-Ge contacts on ZnSe at 300°K.

- (a) 0.05 mA/cm. Vert., 0.05 V/cm Hor., Alloyed at 300°C for  $\frac{1}{2}$  minute.
- (b) 0.05 mA/cm. Vert., 0.02 V/cm Hor., Alloyed at 300°C for 1 minute.
- (c) 0.05 mA/cm. Vert., 0.02 V/cm Hor., Alloyed at 300°C for  $1\frac{1}{2}$  minutes.
- (d) 5.00 mA/cm. Vert., 0.1 V/cm Hor., Alloyed at 350°C for  $\frac{1}{2}$  minutes.

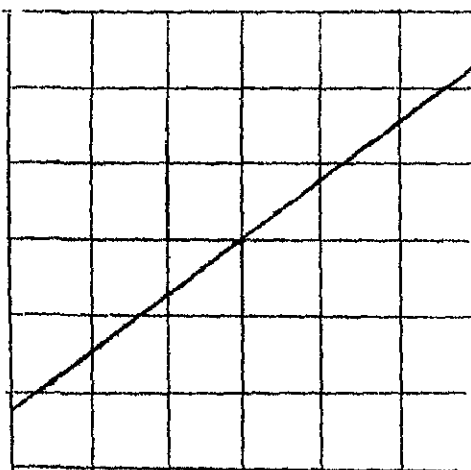




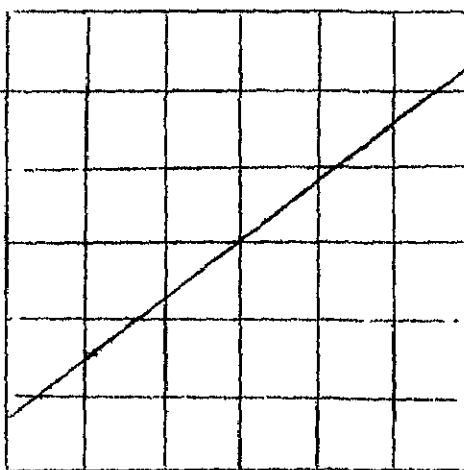
(a)



(b)



(c)



(d)

Figure 3.8: I-V characteristics of In.Ga contacts on ZnSe at 300°K.

- (a) 5 mA/cm. Vert., 0.05 V/cm. Hor., alloyed at 350°C for 1 minute.
- (b) 5 mA/cm. vert., 0.05 V/cm Hor., Alloyed at 350°C for 1½ minutes.
- (c) 5 mA/cm Vert., 0.05 V/cm. Hor., Alloyed at 400°C for ½ minute.
- (d) 5 mA/cm vert., 0.05 V/cm. Hor., Alloyed at 400°C for 1 minute.

250°C for 1/2 minute. Nonlinearity decreased at 300°C and further decreased at 350°C to a great extent. Nonlinearity also decreased when the alloying time was increased and came to a stop when the alloying time was very much increased. At 400°C, the contacts were found to be linear having a contact resistance of 16 ohms between two metal dots. It was seen that this contact resistance decreased to 5 ohms when sample was more carefully lapped.

## CHAPTER 4

### BARRIER STUDIES ON ZINC SELENIDE

When two substances are brought into contact, a redistribution of charge occurs; finally a new equilibrium condition is reached in which the Fermi levels of the two substances are at equal heights. This rule holds not only for contacts between two metals but also for the contact between a metal and n-type or a p-type semiconductor.

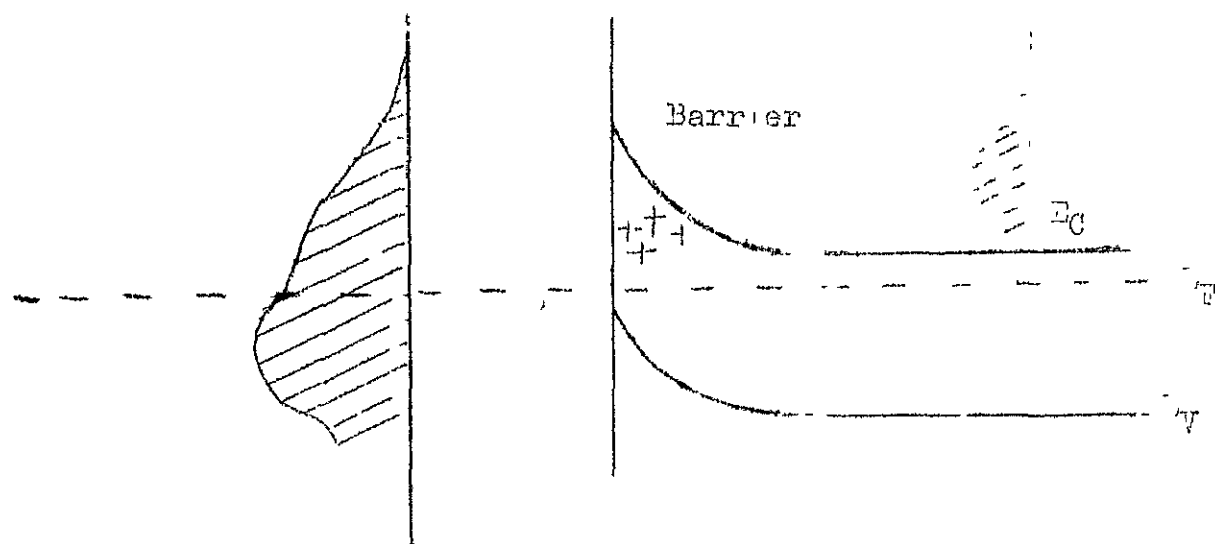
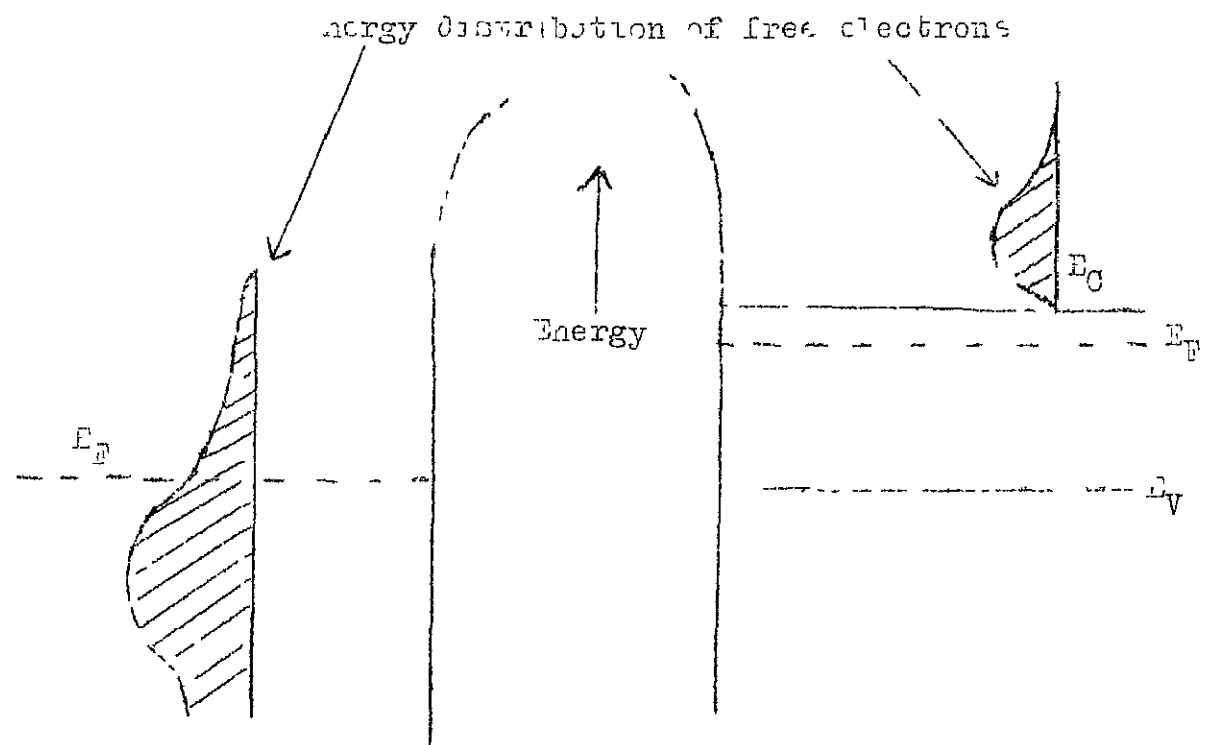
Owing to the redistribution of charge, a dipole layer will be formed at the contact. In a metal-metal contact this dipole layer is always caused by surface charges on both sides of the contact; such a contact is an ohmic contact, since the electrons can move freely from the one metal into the other. In a metal-semiconductor contact, however, the contact may either be ohmic or rectifying. The latter is a contact in which the current flows much more easily in one direction than in opposite direction.

We can see that this is intimately connected with electron energy level diagram of the two substances. Now we shall discuss a contact between a n-type semiconductor and a metal.

In Figure 4.1 is shown a barrier which is formed by the contact difference of potential between the n-type semiconductor and the metal with which it is placed in contact. At the top of the figure the metal and the semiconductor are shown before the contact is made. The Fermi levels of the two do not fall at the same energy. Once the contact is made and the two materials become a single thermodynamic system, there must be single Fermi-level for the system. This is accomplished by a flow of electrons from the body with the higher Fermi level to the body with the lower Fermi level. These electrons distribute themselves over the surface of the contact between the two bodies, giving rise to a dipole layer of surface charge. This dipole layer forms the barrier.

#### Experimental.

The n type ZnSe crystals used in the experiments had bulk doping concentration of  $1.84 \times 10^{16} \text{ cm}^{-3}$ , as calculated from C-V measurements. The resistivity of the crystals was 0.25 ohms cm. Prior to the barrier-metal evaporations, the wafers were lapped to a finish of 1 micron and etched to a smooth surface polish, the etching being carried out for a period of 5 minutes in Bromine methanol solution and then 1/2 minute dip in hot dilute NaOH. Ohmic contacts to the wafers were fabricated by alloying small dots of 25% In-Ga alloy on to one side of the wafer at 400°C. The metal evaporations were carried out in a



Distance into metal

Distance into n type  
semiconductor

Figure 4.1 : Electron energy diagram of metal semiconductor system.

diffusion oil-pumped vacuum system, the pressure was in all cases brought down to  $2 \times 10^{-6}$  torr. Deposition of the metal was through a 'circular mask' to give a circular contact. Electrical connections to the barrier metal were made with a gold wire attached to the barrier metal with the help of silver paint. The device was mounted on a glass plate.

The fabricated devices were subjected to current voltage (I-V) and capacitance voltage (C-V) measurements. Model No. 74C-S18, Boonton capacitance bridge was used for capacitance voltage measurements which has inbuilt voltage supplied to the testing terminals.

#### Electrical Measurements of the Diodes:

##### (a) Forward Characteristics:

Current voltage characteristics of a Schottky barrier diode following thermionic emission diffusion theory<sup>27</sup> is given by

$$J = J_S (e^{qV/kT} - 1) \quad (4.1)$$

$$J_S = A^{**} T^2 \exp\left(-\frac{\phi_B}{kT}\right) ; \quad J = \frac{I}{S}$$

where  $S$  is the diode area,  $A^{**}$  is the Richardson constant,  $T$  is the absolute temperature,  $\phi_B$  is the barrier height,  $k$  is the Boltzmann constant,  $q$  is the electronic charge and  $V$  is the applied voltage.

For  $V > 3kT/q$ , we can write Eq.(4.1) as

$$J = A^{**} T^2 \exp\left(-\frac{\phi_{B0}}{kT}\right) \exp\left(\frac{q(\Delta\phi + V)}{kT}\right)$$

where  $\phi_{B0}$  is the zero field barrier height and  $\Delta\phi$  is the Schottky barrier lowering. Since both  $A^{**}$  and  $\Delta\phi$  are characteristics (for  $V > 3kT/q$ ) is not represented by  $J \sim \exp(qV/kT)$  but rather by

$$J \sim \exp(qV/nkT)$$

where the parameter  $n$  is given by

$$n = \frac{q}{kT} \cdot \frac{\partial V}{\partial (\ln J)}$$

Forward characteristics of Metal-n-ZnSe Schottky barriers are plotted in Figure 4.2 for ten metals. The value of  $n$  is found to be  $1.1 \pm 0.02$ .

Reverse Characteristics:

A slight voltage dependence of the reverse characteristics is observed which is apparently due to image force lowering<sup>28</sup>. In the reverse direction,

$$J_r \simeq J_s \text{ (for } V_r > 3kT/q)$$

$$= A^{**} T^2 \exp\left(-\frac{\phi_B}{kT}\right) \exp\left(+\frac{(q\sqrt{qE/4\pi\epsilon_s})}{kT}\right) \quad (4.2)$$

where

$$E = \sqrt{\frac{2qN_D}{\epsilon_s}} (V_i + V_r - kT/q) ;$$

$V_i$  is the built in voltage and  $\epsilon_s$  is the dielectric constant.

If the barrier height  $\phi_B$  is reasonably smaller than the bandgap such that the depletion layer generation-recombination current is small in comparison with the Schottky emission current then the reverse current will increase gradually with the reverse bias as given by Eq.(4.2).

Reverse characteristics of Schottky barrier diodes made on ZnSe are shown in Figure 4.3. If reverse characteristics can be explained in terms of image force barrier lowering, a plot between  $\ln I$  and  $(V_1 + V_r - kT/q)^{\frac{1}{2}}$  should be found to be a straight line. These plots have been drawn in Figure 4.4(a) and 4.4(b). The slope of these lines can be used to find out the dielectric constant of ZnSe. The slopes for different metals used are found to be different. An average value of 3.00 for dielectric constant has been calculated from these graphs.

#### Capacitance Voltage Measurements:

Capacitance voltage characteristics can be used to determine the barrier height of a metal-semiconductor contact. It has been discussed in detail by Goodman<sup>29</sup>. Using the simple model, the following relations are obtained.

$$1/C^2 = \frac{2(V_1 - V)}{N_A^2 q \epsilon_s} \quad (4.3)$$



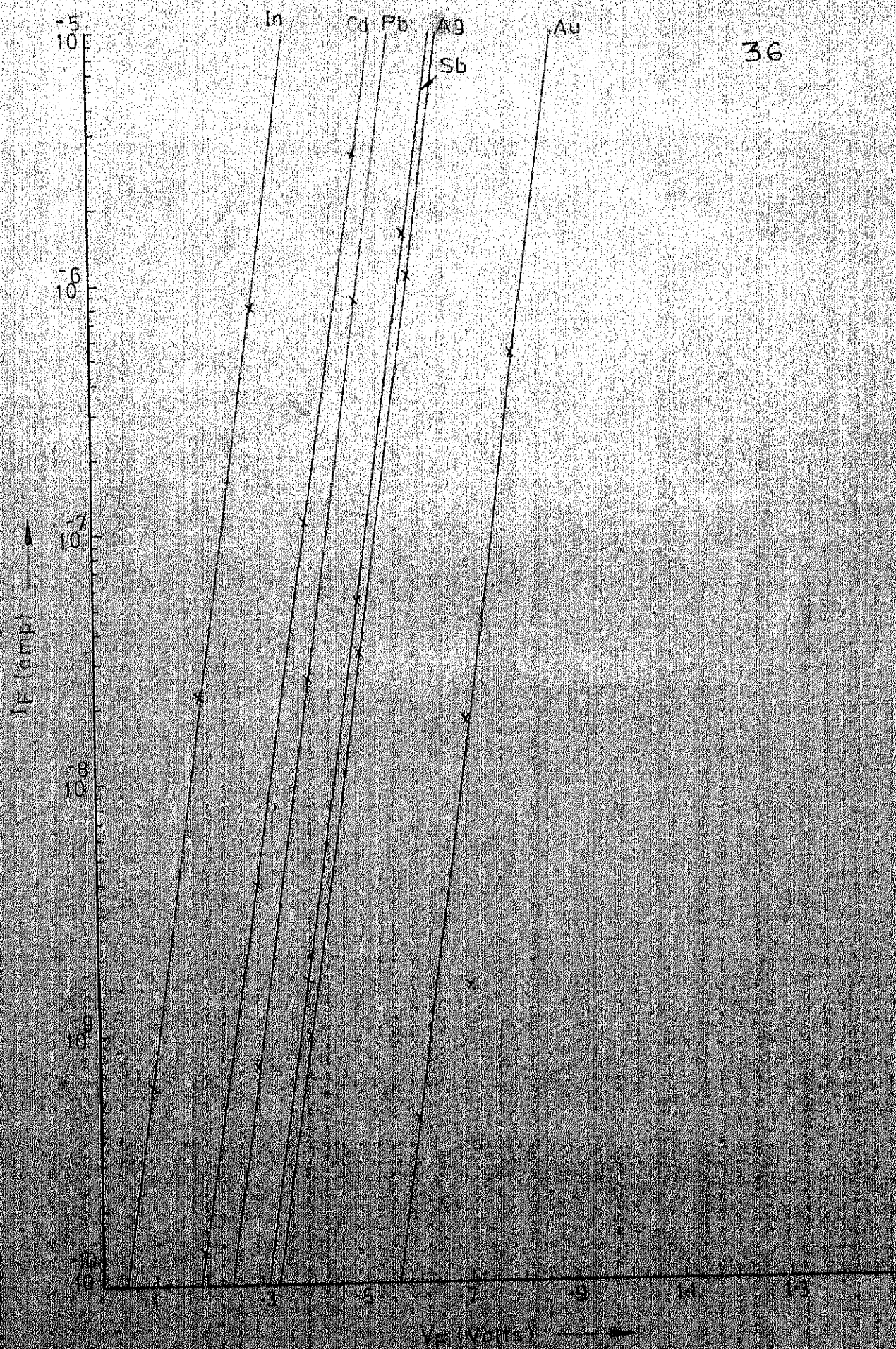


FIG. 4-2(a)



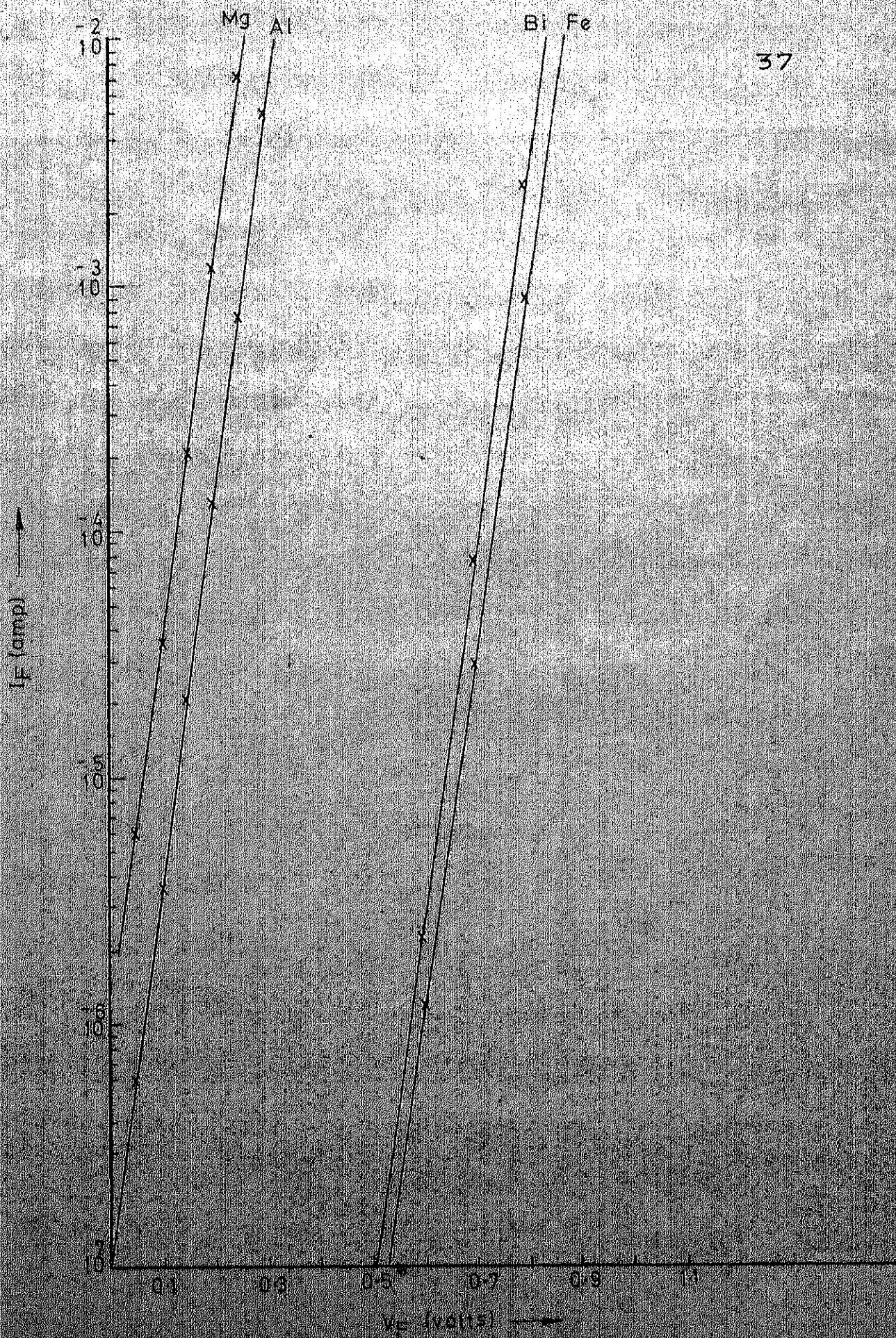


FIG. 42(b)



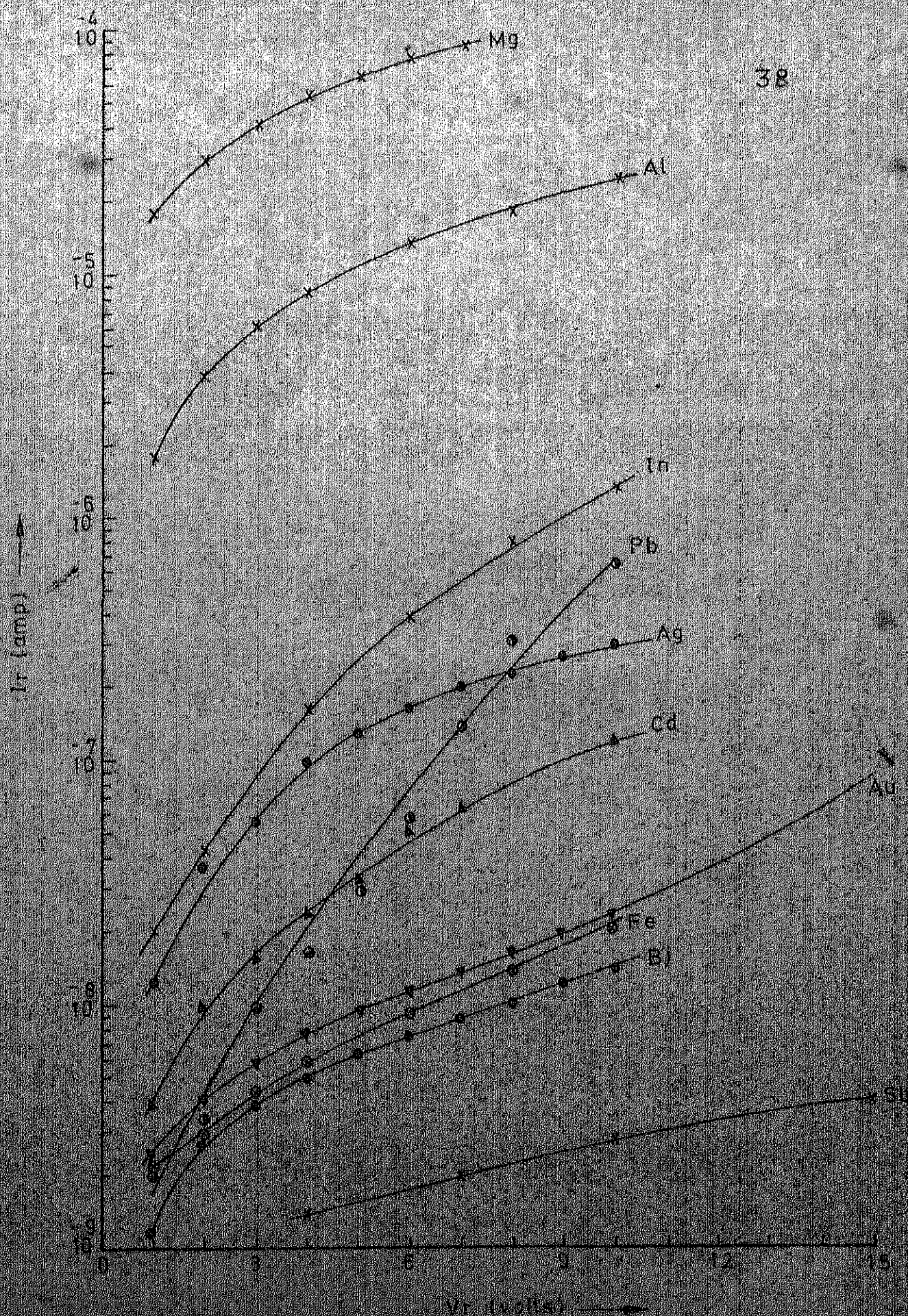


FIG. 4-3



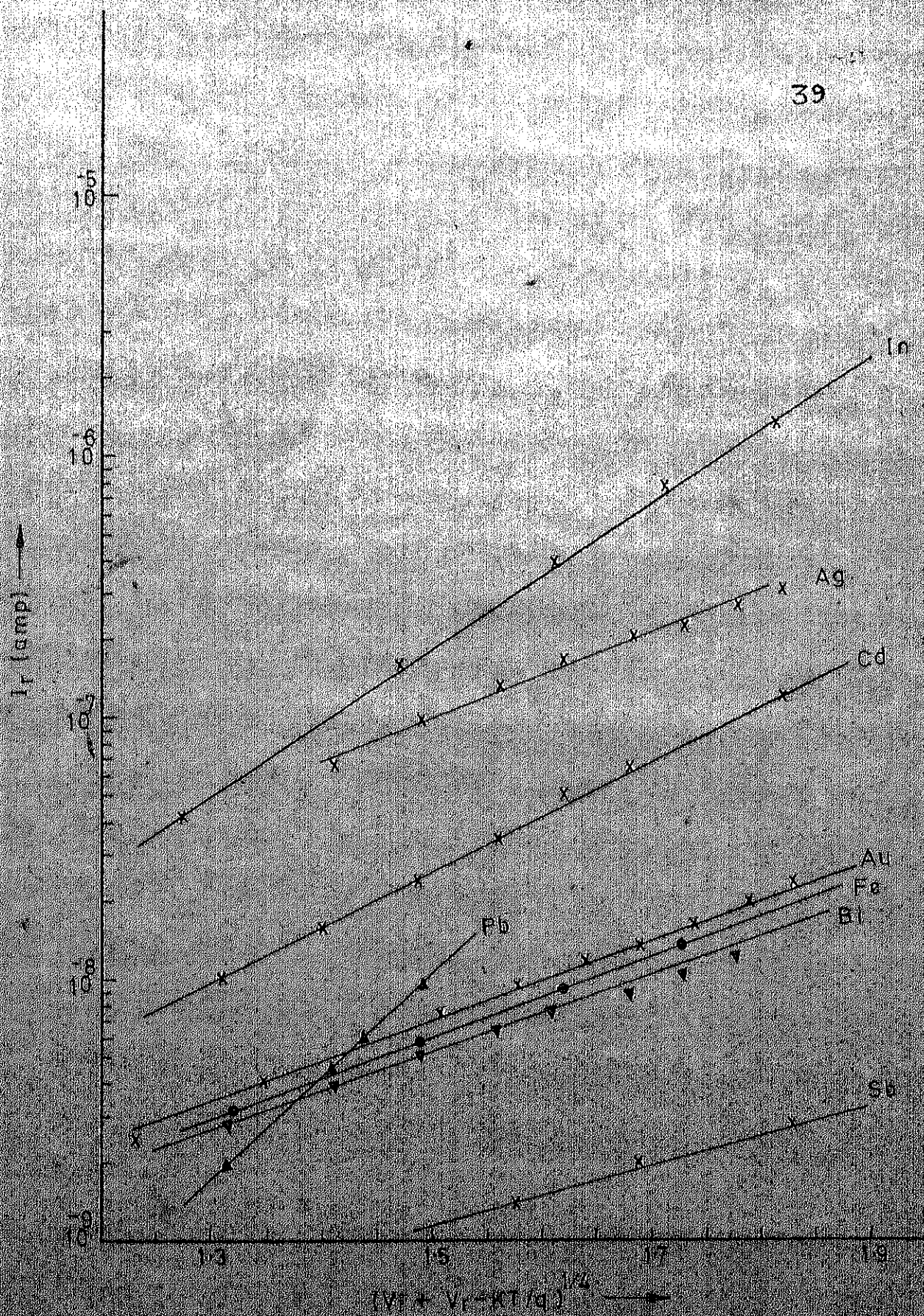


FIG. 4.4(a)



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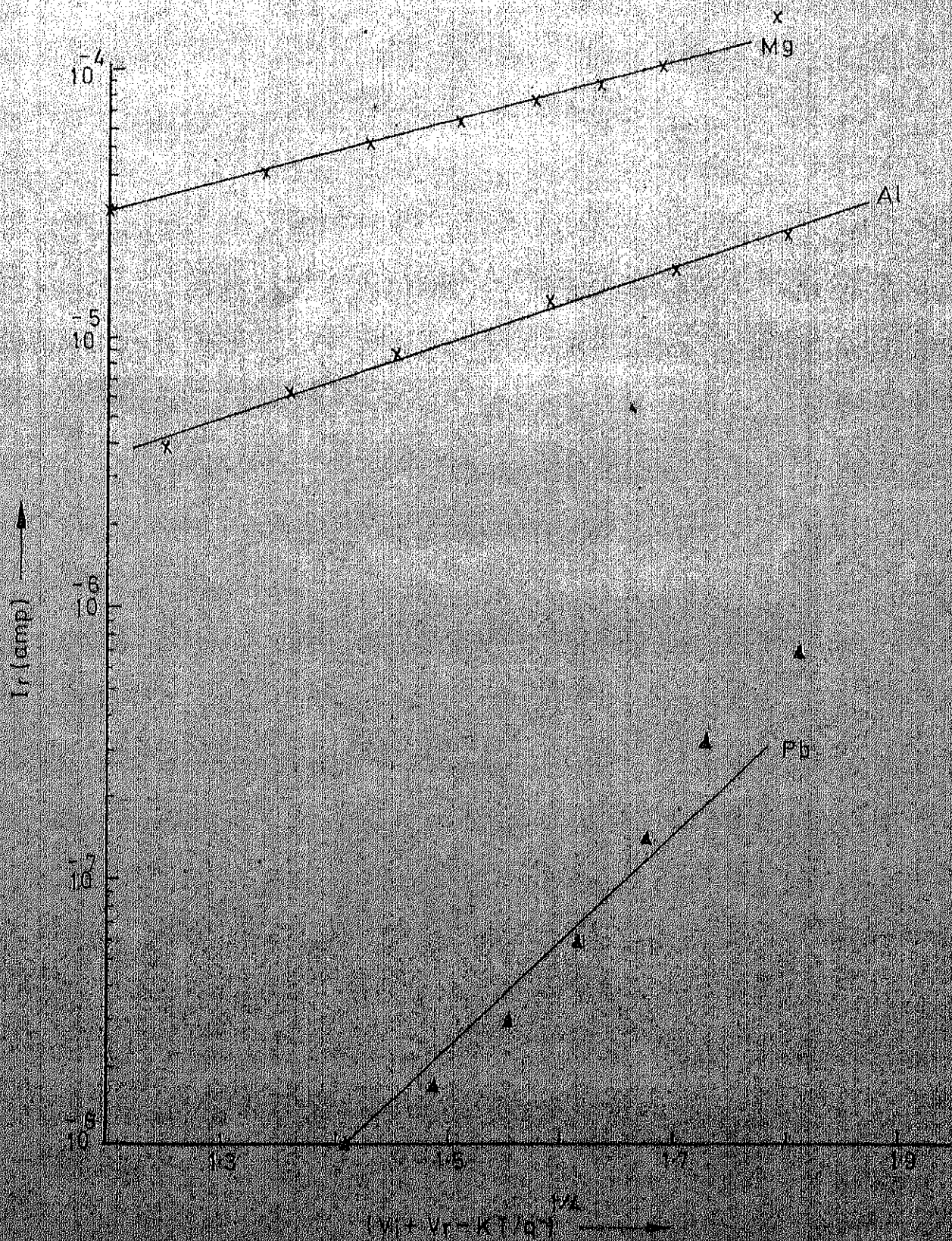


FIG. 4.4(b)



4)

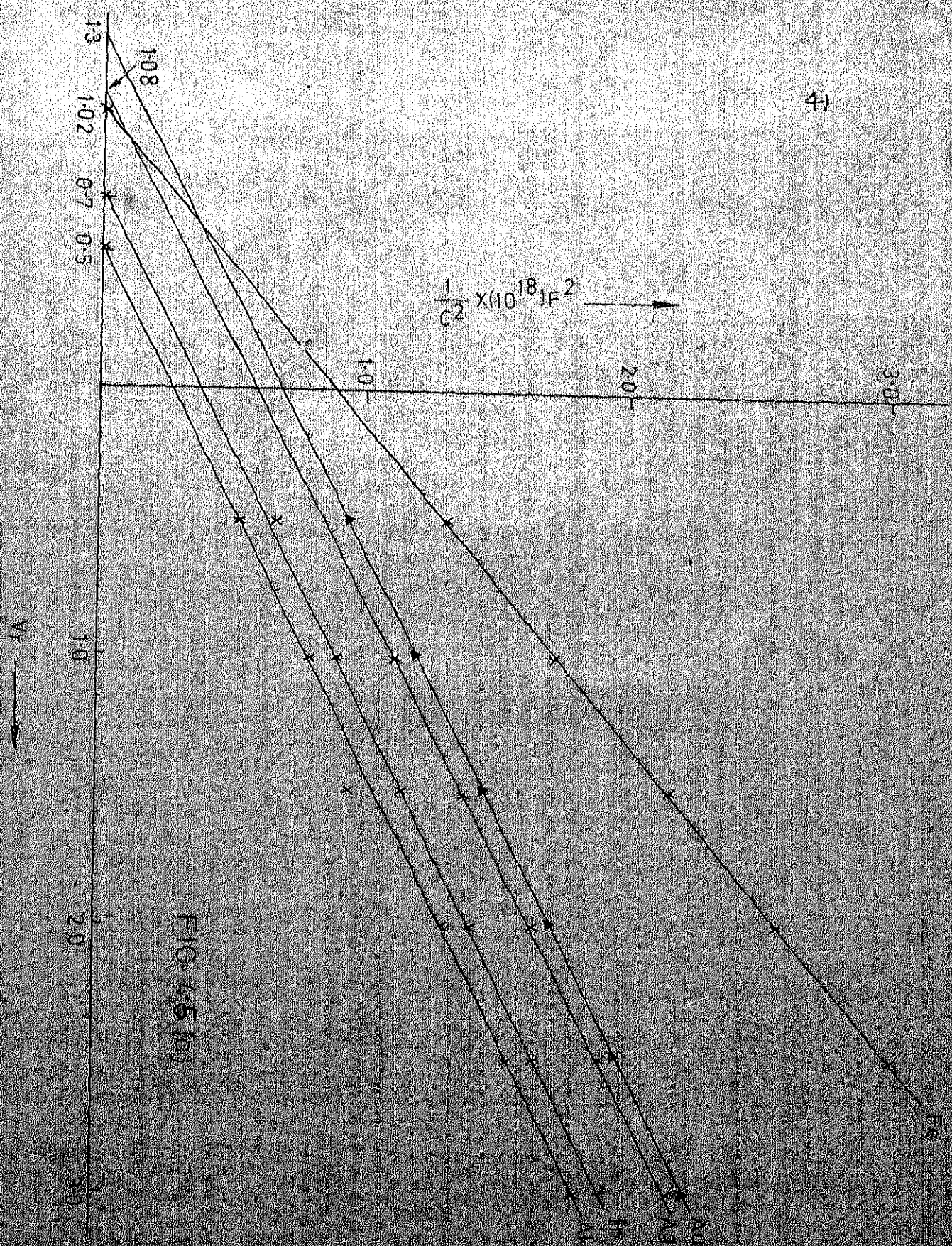


FIG. 4.5 (b)



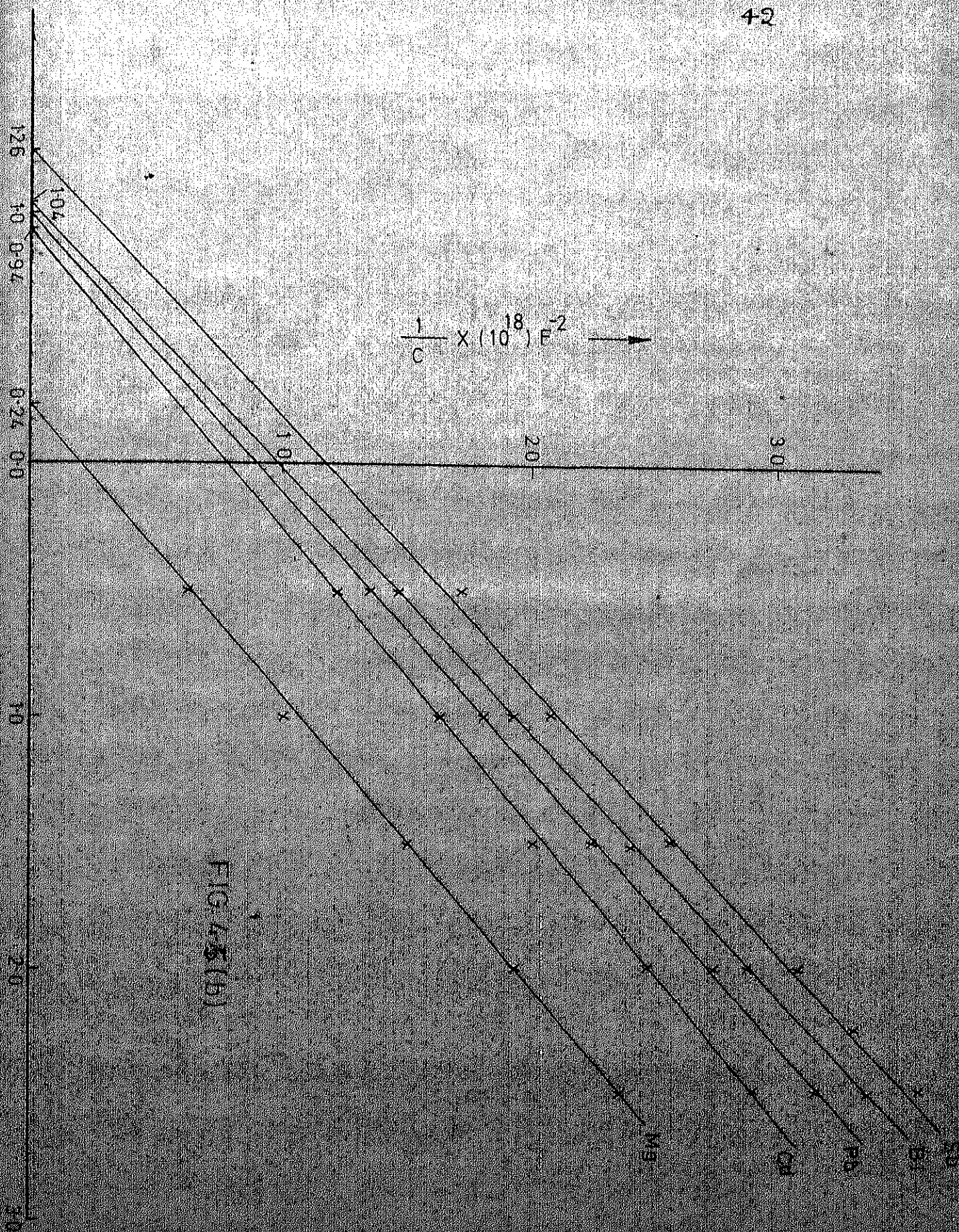


FIG. 4-5(B)



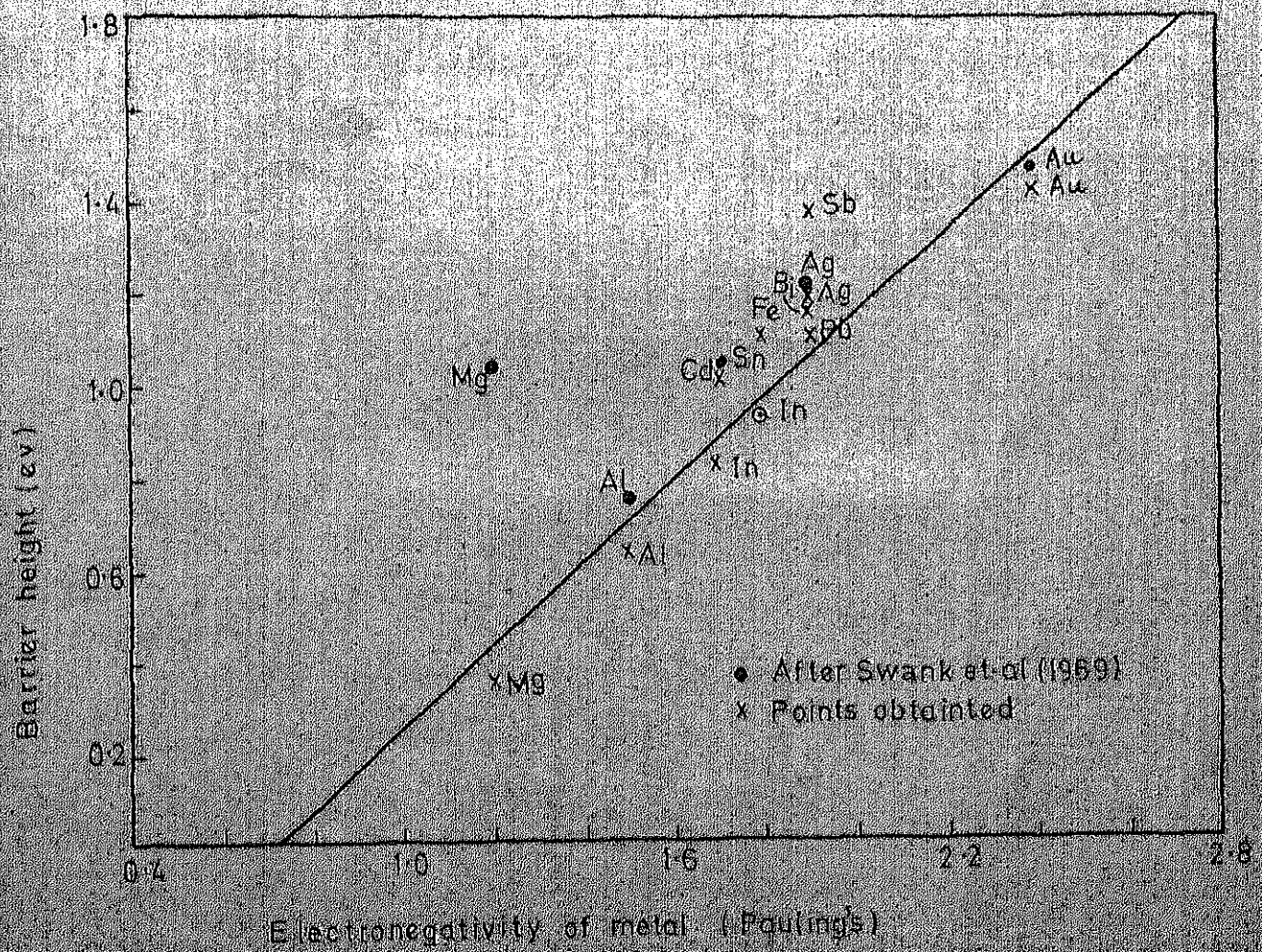


FIG. 4.6



$$N = -2 / (A^2 q \epsilon d(1/C^2)/dV) \quad (4.4)$$

$$\phi_B = q V_1 + \xi + kT$$

where  $C$  is the differential capacitance of the contact,  $V_1$  is the built-in voltage of the space charge region,  $V$  is the applied bias voltage,  $N$  the uncompensated donor concentration,  $\epsilon$  the dielectric constant of the semiconductor,  $\xi$  the depth of the Fermi level below the bottom of the conduction band in the bulk of the semiconductor.

C-V plot can also be used for calculating the value of  $N$  using Eq.(4.4).

Barrier heights have been calculated using C-V plot for ZnSe Schottky barrier. The values of barrier heights are given in Table 4.1. The value of donor concentration equal to  $1.84 \times 10^{16}$  has been found from C-V plots.

Barrier Height from I-V Measurement:

Value of Richardson constant  $A^{**}$  was calculated for Au barrier, taking the barrier height calculated from C-V measurement. Taking this value of  $A^{**}$ , barrier height for other metal barriers is calculated. The results are given in Table 4.1.

Table 4.1

S No.	Metal	Contact Area (cm <sup>2</sup> )	$\phi_B$ (eV) (C-V)	$\phi_B$ (eV) (I-V)
1	Au	4.93	1.42	
2	Ag	4.93	1.20	1.3
3	In	4.93	0.82	0.892
4	Al	4.93	0.62	0.725
5	Se	3.14	1.14	1.207
6	Sb	3.14	1.38	1.198
7	Pb	3.14	1.16	1.192
8	Tb	3.14	1.12	1.125
9	Cd	3.14	1.06	1.09
10	Mg	3.14	0.36	0.653

Barrier height on ZnSe

## CHAPTER 5

## CONCLUSION

Good ohmic contacts can be made on ZnSe crystals using 25% In-Ga alloy. Contact Resistance very much depends on the surface preparation of the Semiconductor. In the present work, ZnSe samples were lapped with 1 micron  $\text{Al}_2\text{O}_3$  powder. More smooth finish can be obtained by using more fine powder with pellow cloth.

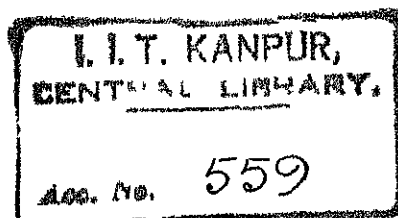
In-Ga contacts are liquid at room temperature and therefore are not useful for practical devices. To increase the strength of contacts, silver past was mixed into the contact, after In-Ga had been alloyed to ZnSe. This gives some hardness to contacts but contacts are very irregular.

Barrier heights on ZnSe were measured. An attempt was made to correlate barrier height with metal workfunction, taking the values of workfunction available in literature. Very poor correlation was obtained. The correlation of barrier height with electronegativity, however, is fairly good.

## REFERENCES

1. H. L. Henisch, Rectifying Semiconductor Contacts, p.183, Oxford University Press, Oxford (1957).
2. J. Bardeen, Phys.Rev.71, 717 (1947).
3. I.G. Spitzer and C.A. Mead, J. Appl.Phys.39, 3061 (1963).
4. A. J. Goodman, J. Appl. Physics, 35, 575(1964).
5. C.A. Mead, Solid State Electronics, 9, 1023(1966).
6. M. Ven and C.A. Mead, Appl.Phys. Letters 7, 8(1965).
7. C. A. Mead, Physics Letters, 18, 218 (1965).
8. R. A. Swank, H. Aren and J. Z. Devine, J. Appl. Physics, 40, 89 (1969).
9. R. K. Swank, Phys. Rev. 153, 844 (1967).
10. J. D. Levine and P. Mark, Phys. Rev. 144, 751(1966).
11. Pashinkvi, L.S., et.al., Kristallographia, 5, 261(1966).
12. Kornceva, I.V., Soviet Phys. Cryst. 6, 505 (1962).
13. Segall, B. and Marple, D.T.F., Physics and Chemistry of III VI Compounds, pp.319-381 (H. Aven and J.S. Prener eds.) North Holland, Amsterdam, 1967.
14. Marple, D.T.F., J. Appl. Phys. 35, 539 (1964).
15. Marple, D.T.F., J. Appl. Phys. 35, 1879 (1964).
16. Pauling, L., The nature of the chemical bond, 3rd Edition, McGraw-Hill, New York, 1960.
17. A.G. Fischer and W.H. Fonger, "Investigation of two-carrier injection electroluminescence", Final Report AD 647087 (December 14, 1966).
18. T.O. Yep and R.J. Archer, Hewlett Packard Company, "Investigation and Development of Semiconductor Metal Electrode", Final Report, AF19 (628) 5946 (Aug. 1967).

19. J.W. Mellor, Handbook on Chemistry.
20. M.Aven and B.Segall, Phys. Rev., 130, 81 (1963).
21. M. Aven, Appl. Phys. Letters, 7, 146 (1965).
22. A Najima and S. Ibuki, Jap. J. of Appl.Phys., 5, 253 (1966).
23. G.W. Ludwig and M. Aven, J. of Appl.Phys., 38, 5326 (1967).
24. D.L. Feucht and A.G. Milnes, "Semiconductor Hetero-junction Studies", AFCRL-68-0348, Electrical Engg. Dept., Carnegie Millon University, Pittsburgh, Pa. June 1968.
25. G.W.Ludwig in II-VI Semiconducting Compounds, International Conference, Edited by G. Thomas, W.A. Benjamin, Inc., New York, 1289 (1967).
26. Culow, et.al., Hewlett-Packard Company, Final Report, AF 19(628), 5946, (August 1967).
27. C.R. Growell and S.M. Sze, Solid State Electronics, 9, 1035 (1966).
28. W. Schottky, Naterwiss, 26, 843 (1938).
29. A.M. Goodman, J. Appl. Phys. 34, 329 (1963).
30. M.S. Tyagi, Unpublished Report on Ohmic Contacts to II-VI Compounds.



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